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New sensitive layers for surface acoustic wave gas sensors based on polymer and carbon nanotube composites

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Abstract

Surface acoustic wave (SAW) gas sensors based on carbon nanotube polymer composites as sensitive layers were investigated for the detection of low concentrations of volatile organic compounds as octane and toluene. Several nanocomposites based on polyepichlorohydrin (PECH) and polyetherurethane (PEUT) with different percentage of multiwalled carbon nanotubes (MWCNT) were tested to study the effect of MWCNTs in the response of sensors.

Keywords: SAW gas sensors; Carbon nanotubes; composite; polyepichlorohydrin; polyetherurethane; volatile organic compounds

1. Introduction

Carbon nanotubes (CNTs) exhibit remarkable structural and physical properties that make them potentially useful for applications including nanoelectronics, multifunctional composite materials, or field emission devices [1]. Their high surface area, size and hollow geometry also make them promising candidates to be used as components of gas and chemical sensors [2,3].

SAW devices have very good characteristics as chemical gas sensor due to their small size, low cost, fast response and high sensitivity. Composite materials based on carbon nanotubes and some other materials (polymers, metal nanoparticles, oxide nanoparticles) are promising candidates to obtain new sensitive layers for gas detection [4,5].

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SAW sensors consist of a set of interdigited electrodes (IDTs) patterned onto the surface of a piezoelectric substrate (quartz, lithium niobate, and lithium tantalate) forming a delay line (DL) and a sensitive layer. The basic operating principle of SAW sensors is the reversible adsorption of gases by an adsorbent coating which is sensitive to the gas to be detected. The gas is adsorbed by the sensitive layer resulting in a mass increase which alters the surface wave velocity in the device. The velocity changes are measured indirectly with good precision using the device as the resonant element in a delay line (DL) oscillator circuit and measuring the frequency shifts due to the gas adsorption.

In this work an array of five SAW sensors have been developed with composite (polymers and carbon nanotubes) as sensitive layers for the detection of volatile organic compounds (VOCs) at room temperature. Several nanocomposites based on polymers (PECH and PEUT) with different percentage of MWCNTs were tested to study the effect of MWNTs in the response of the sensors.

2. Experimental

SAW sensor consists of a delay line made on a piezoelectric quartz substrate (ST-X cut) and a sensitive layer (composite) deposited between the IDTs. The IDTs were made of aluminium obtained by RF sputtering using photolithographic techniques, with a 200 nm thickness and a finger width and spacing among them of 5 μm, being therefore the wavelength, λ, of 20 μm. The dimensions of each device were 9 mm × 4 mm × 0.5 mm, and the area of sensitive layer was 1mm ×1 mm. These parameters were optimized in previous reports [6,7].

Two polymers were used in order to preparation of the composites: polyepichlorohydrin (PECH) and polyetherurethane (PEUT). First, solutions of PEUT in dichoromethane and PECH in chloroform were prepared. Beside, pre-dispersion of multi-walled carbon nanotubes (MWCNTs, Arkema S.A.) in the same solvents are obtained by sonication. Then, the solutions were mixed also by ultrasounds in order to obtain 2 and 5 wt.% MWCNT nanocomposites. Finally, these solutions were deposited onto quartz substrate by airbrush spraying using a metallic mask.

The sensor array is formed by five SAW devices (Table 1), one of them is used as reference (without sensitive layer) to compensate common error sources such as small changes of room temperature and pressure. The response measured is the difference between the frequency of every sensor and that of the reference device.

Table 1: Tested Sensors

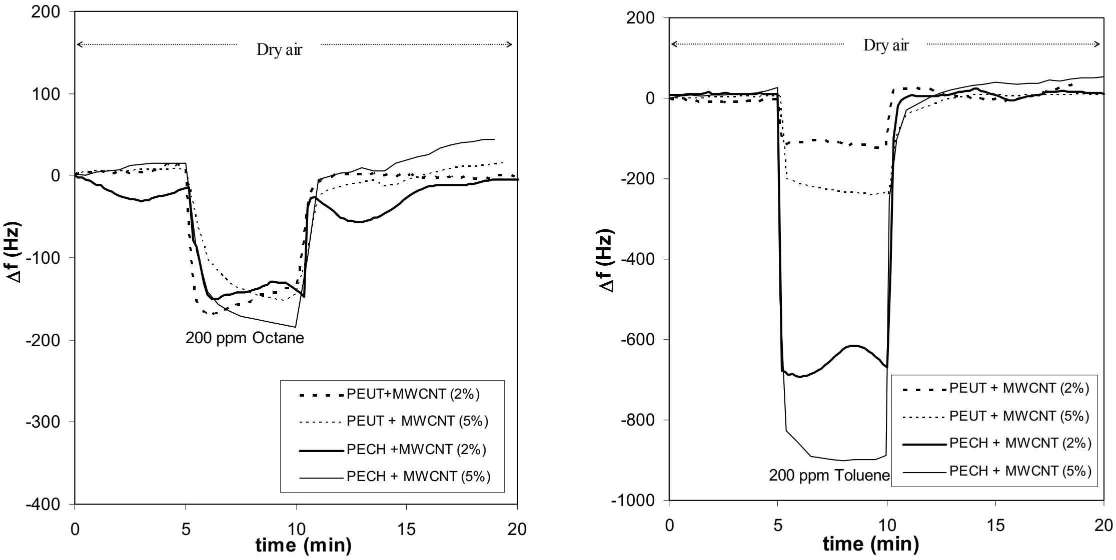
Sensor	Sensitive layer
S0 (reference)	None
S1	PEUT-MWCNT (2%)
S2	PEUT-MWCNT (5%)
S3	PECH-MWCNT (2%)
S4	PECH-MWCNT (5%)

Detections were carried out in dry air at room temperature, with a constant flow of 200 mL/min and exposure times of 5 min. The concentrations used for octane and toluene were in the range of 25–200 ppm. Detection experiments for other pollutant gases (NO_2, NH_3, CH_4, H_2, dimethylamine, trimethylamine and CO) were also performed. Concentrations of these gases ranged from a few ppm

(NO_2) to hundreds of ppm (NH_3, CH_4, dimethylamine, trimethylamine and CO), and up to 2% for H_2. Gas concentrations were controlled by means of mass flow controllers.

3. Results and discussion

The tested sensors were sensitive to octane and toluene and they presented a higher response to toluene than to octane (Fig. 1) at room temperature. Moreover, the sensors with higher percentage of CNTs (5%) showed an increase in their response to both gases (Fig. 1).



(a) (b)

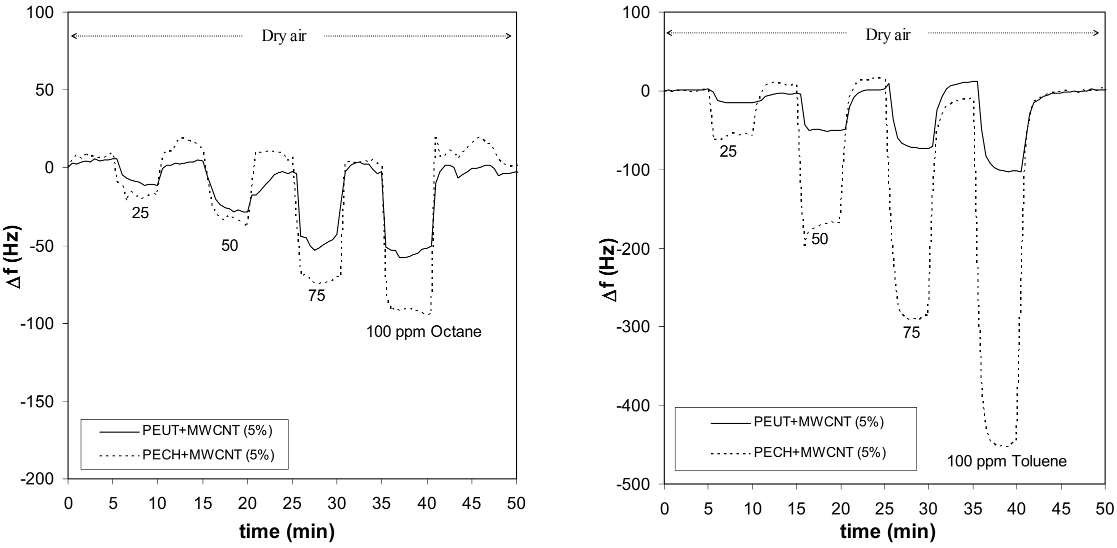
Fig. 1: Sensor responses at 200 ppm to (a) octane and (b) toluene at room temperature.

Fast response (30-40 s) and recovery time (50-60 s) were obtained at room temperature. The sensors show a linear relation between gas concentration and frequency response (Δf=cte.[concentration]) (Fig. 2). It can also be seen that the sensors repeatability (the difference in sensor signal in air before and after cycling in VOCs) is good and the VOCs are completely removed from the sensitive layers in every cycle.

Detections of other pollutant gases (NO_2, NH_3, CH_4, H_2, dimethylamine, trimethylamine and CO) were also performed and the sensors did not modified their frequency by the presence of these gases.

4. Conclusions

The sensing properties of the different composites based on polymers and carbon nanotubes have been investigated by SAW gas sensors. Sensitive layers were obtained by simply airbrushing dispersions on quartz substrate. High sensitivity of the sensors to toluene and octane has been obtained at room temperature. The introduction of small percentages of MWCNT into the polymer increased the adsorption of toluene but did not modify the response to octane. These composites present new possibilities to improve the sensitivity and selectivity of SAW sensors.



(a) (b)

Fig. 2: Dynamic response of sensors to different concentration of (a) octane and (b) toluene, at room temperature.

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